

19



Europäisches Patentamt
European Patent Office
Office européen des brevets

11 Publication number:

**0 242 925
A2**

12

EUROPEAN PATENT APPLICATION

21 Application number: 87200743.0

22 Date of filing: 17.04.87

51 Int. Cl.4: **C10M 105/62 , C10M 111/02 ,
//C10N40/24,(C10M111/02,105:-
62)**

30 Priority: 21.04.86 JP 90098/86
18.09.86 JP 218102/86
26.08.86 JP 198108/86

43 Date of publication of application:
28.10.87 Bulletin 87/44

84 Designated Contracting States:
BE DE FR GB IT NL

71 Applicant: The Nisshin Oil Mills, Ltd.
23-1, 1-chome Shinkawa Chuo-ku
Tokyo(JP)

Applicant: NIPPON STEEL CORPORATION
6-3 Otemachi 2-chome Chiyoda-ku
Tokyo 100(JP)

72 Inventor: Tanikawa, Keiichi
34-7, Konandai 1-ch. Konan-ku
Yokohama-shi Kanagawa(JP)
Inventor: Higaki, Yuzo
1143-3, Kogasaka
Machida-shi, Tokyo(JP)
Inventor: Goto, Hiroyuki
27-9, Mori 6-chome Isogo-ku
Yokohama-shi Kanagawa(JP)

24 Representative: Noz, Franciscus Xaverius, Ir.
et al
Boschdijk 155
NL-5612 HB Eindhoven(NL)

54 Cold-rolling oils for steel plates.

57 Lubricating oils for rolling of steel plates, which are composed of synthetic ester compounds obtainable from tri- or higher-valent alcohols having tertiary nitrogen such as isocyanuric derivatives or ethylene oxide addition products of ethylenediamine and fatty acids, possess well-balanced rolling lubricating properties and mill cleanability at a high level.

EP 0 242 925 A2

Xerox Copy Centre

Cold-Rolling Oils for Steel Plates

BACKGROUND OF THE INVENTION

1. Field of the Invention

5

The present invention relates to a rolling oil having high lubricating properties and high mill cleanability, that is, a cold-rolling oil for steel plates, which excels in lubricating and annealing properties.

10 2. Related Art Statement

Cold-rolling oils used for thin steel plates are generally broken down into two types, one based on animal and vegetable oils and fats (such as tallow and lard, soybean oil, colza oil, palm oil and coconut oil) and the other on mineral oils. Recent demands for energy saving and improvements in productivity lead to
15 higher speed rolling, higher reduction-ratio rolling and mill clean rolling. The rolling oils based on animal and vegetable oils and fats are suitable for high-load and -speed rolling. However, when as cold-rolled steel plates are directly annealed without degreasing oily deposits thereon, it is likely that they may be contaminated on their surfaces in the annealing step. That is, such rolling oils are suitable in view of lubricating properties, but are unsuitable in view of mill cleanability.

20 When cold rolling is carried out with the rolling oils based on mineral oils, on the other hand, excellent mill cleanability is achievable, since as cold-rolled thin steel plates can be directly annealed without any surface contamination. However, such rolling oils lack in high-load and -speed rolling properties.

For use, oilness improvers such as animal and vegetable oils and fats, fatty acids (capric, lauric, myristic, stearic, oleic and linolenic acids) or esters (synthetic esters such as monoesters, diesters or polyol
25 esters wherein the alcoholic components are trimethylolpropane, pentaerythritol and 2-ethylhexyl alcohol) as described in "Oil Chemistry", No. 73-11, pages 695-706 are generally added to the rolling oils based on mineral oils so as to enhance their rolling lubricating properties. However, the amount of such improvers added is regulated to a narrow range of the required minimum limit so as to retain mill cleanability. As mentioned above, various investigations have been made of cold-rolling oils capable of satisfying high
30 lubricating properties and high mill cleanability at the same time (see for instance Japanese Patent Laid-Open Publication Nos. 56-135600 and 59-80498). However, there is not still found any rolling oil meeting both properties in a well-balanced state and at a higher level.

35 SUMMARY OF THE INVENTION

The present invention provides cold-rolling oils for steel which make a contribution to improvements in productivity as expressed in terms of energy saving and reductions in the number of the steps involved, and which are stable with respect to heat and mechanical shearing occurring at high speeds and pressures
40 and even with respect to chemical reactions such as oxidation, decomposition and polymerization. The cold-rolling oils according to the present invention are easily volatilized off in the annealing step without giving rise to thermally decomposed residues, and combine steel-plate's surface cleanability (mill cleanability) with high lubricating properties.

More specifically, the cold-rolling oils for steel according to the present invention are composed mainly
45 of the esterified products of tri-or higher-valent alcohols selected from amino alcohols having tertiary nitrogen and fatty acids having six or more carbon atoms, have high lubricating properties and high mill cleanability, and make it possible to effectively carry out rolling of thin steel plates and annealing of the steel plates without degreasing the same.

50

DETAILED DESCRIPTION OF THE INVENTION

The synthetic esters referred to in this disclosure are "molecularly designed" and synthesized to this end. In recent years, synthetic esters have been employed as base oils of, or additives for, rolling oils. However, most of synthetic esters used as cold-rolling oils are not synthesized to this end, and are often selected from existing synthetic esters employed as engine oils, hydraulic working oils or other lubricant. Thus, they fail to meet satisfactorily both high lubricating properties and high mill cleanability.

The synthetic esters according to the present invention have the properties suitable for cold-rolling oils, i.e., combine high lubricating properties with high mill cleanability, and are "molecularly designed", as mentioned below.

For instance, the tri- or higher-valent alcohols having tertiary nitrogen used in the present invention include triethanolamine, triisopropanolamine, N,N-bis(2-hydroxypropyl)ethanolamine, N,N-bis(2-hydroxyethyl)-isopropanolamine, triethanolamine tris-glycoether, triisopropanolamine tris-glycoether, tris(2-hydroxyethyl)isocyanurate, N,N,N',N'-tetrakis(2-hydroxyethyl)ethylenediamine, and N,N,N',N'-tetrakis(2-hydroxypropyl)ethylenediamine.

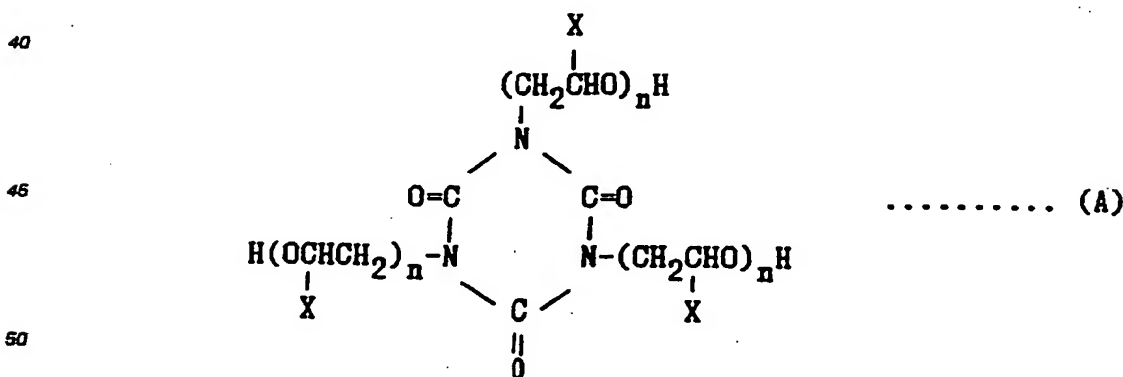
In accordance with the present invention, particularly preferable tri- or higher-valent alcohols having tertiary nitrogen are isocyanuric derivatives expressed in terms of the general formula (A) to be given later or polyvalent alcohols expressed in terms of the general formula (B) to be given later, wherein the mother nucleus is formed by an alkylene (or phenyl or cyclohexyl) diamine that is a tetravalent alcohol.

The fatty acids to be used in the present invention may include straight or branched-chain, saturated or unsaturated and natural or synthetic fatty acids having six or more carbon atoms such as those represented by hexanoic, octanoic, decanoic lauric, myristic, palmitic, stearic, arachinic, behenic, montanic, palmitoleic, oleic, erucic, ricinoleic, hydroxystearic, linoleic, linolenic, isooctylic, isodecanoic, isolauric, isomyristic, isopalmitic, isostearic and isoarachinic acids.

It has been found that, with the esterified products of the specific alcohols and fatty acids having 5 or less carbon atoms, it is impossible to enhance to a sufficient degree the lubricating properties in cold-rolling of steel plates. This is because the present invention is limited to fatty acids having six or more carbon atoms. Although no particular limitation is placed upon the upper-limit number of carbon atoms contained in the fatty acids used, on the other hand, fatty acids having 30 or less carbon atoms are preferred in view of commercial availability and price.

The esterified products according to the present invention may be synthesized by esterification of the tri- or higher-valent alcohols having tertiary nitrogen and the fatty acids, which may be effected in the presence or absence of catalysts in any conventional manner.

One preferred esterified products according to the present invention are the esters of the isocyanuric derivatives having the aforesaid general formula (A) and the fatty acids having six or more carbon atoms, that is, the esterified products of the isocyanuric derivatives of the general formula (A) and the fatty acids having six or more carbon atoms, expressed in terms of the following general formula (C):



wherein X is H or CH₃, and n is an integer of 1 to 10, and R-COOH (C)

wherein R, stands for an alkyl, alkenyl, hydroxyalkyl or hydroxyalkenyl group having at least five carbon atoms.

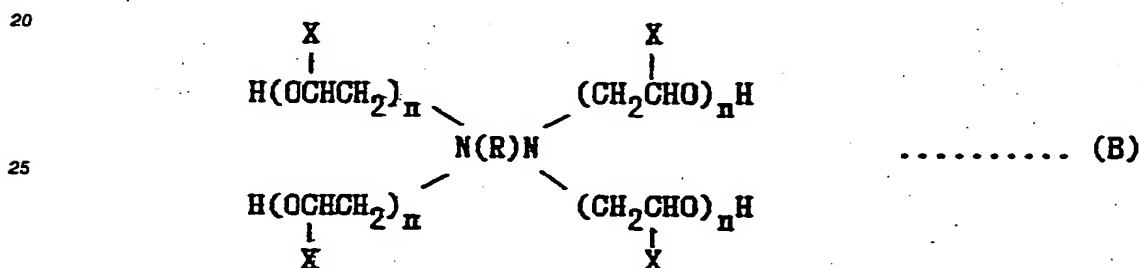
Of the nitrogen-containing polyols (isocyanuric derivatives) having the general formula (A), tris(2-hydroxyethyl)isocyanurate wherein $n = 1$ and $X = H$ is particularly advantageous for the industrial lubricating oils of the present invention, since it is easily commercially available and inexpensive.

No particular limitation is imposed upon the degree of esterification with the fatty acid. It is desired, however, that one mole of tris(2-hydroxyethyl)isocyanurate be esterified with preferably at least 1.5 moles, more preferably at least 2 moles of the fatty acid on the average.

In the nitrogen-containing polyols (isocyanuric derivatives) of the general formula (A), n should preferably be an integer of 1 to 10. It is to be noted, however, that the number n is defined in terms of an averaged number of moles. In some cases, the averaged number of 3 may include 4, since there is then a distribution in the number of addition moles of ethylene or propylene oxide. That is, n is strictly an averaged number which should preferably be not more than 10 in the present invention. If n exceeds 10, the lubricating properties to be achieved then deteriorates.

In general, an increased n allows hydrophilic nature to be afforded to lubricants per se, which then acquire self-emulsifiability or dispersibility.

Another preferred esterified products according to the present invention are the esters of the tetra-valent alcohols of the aforesaid general formula (B) and the fatty acids having six or more carbon atoms, that is, the esterified products of the nitrogen-containing polyols of the general formula (B) and the fatty acids having six or more carbon atoms, expressed by the general formula (C).



wherein X is H or CH_3 , n indicates an integer of 1 to 10, and R stands for an alkyl, having 2 to 6 carbon atoms, phenyl or a cyclohexyl group, and R_1-COOH (C)

The nitrogen-containing polyols of the general formula (A) may be obtained by adding the predetermined amount of ethylene or propylene oxide to ethylenediamine, hexylenediamine, phenyldiamine, cyclohexyldiamine and the like. In particular N,N,N',N' -tetrakis(2-hydroxypropyl)ethylenediamine, wherein $R = C_2H_5$, $n = 1$ and $X = CH_3$, is advantageous for the industrial lubricating oils of the present invention in view of commercial availability and price.

No particular limitation is imposed upon the degree of esterification with the fatty acid. It is desired, however, that one mole of N,N,N',N' -tetrakis(2-hydroxypropyl)ethylenediamine be esterified with preferably at least 2 moles, more preferably at least 3 moles of the fatty acid on the average.

It is to be understood that the reasons why the polyols are limited to ethylene or propylene oxide addition products are that higher alkylene oxide addition products such as butylene oxide addition products are so commercially expensive that difficulty is experienced in obtaining them.

In the nitrogen-containing polyols of the general formula (B), n should preferably be an integer of 1 to 10. Polyols, wherein n is more than 10, have an increased molecular weight and decreases in lubricating properties with an increase in the number of ether bonds. It is to be noted, however, that the number n is defined in terms of an averaged number of moles. In some cases, the averaged number of 3 may include 4, since there may then a distribution in the number of addition moles of ethylene or propylene oxide. In short, n is strictly an averaged number which should preferably be not more than 10 in the present invention. If n exceeds 10, the lubricating properties to be achieved then deteriorates.

In general, an increased n allows hydrophilic nature to be afforded to lubricants per se, which then acquire self-emulsifiability or dispersibility.

The nitrogen-containing polyols, which are the starting material for synthesizing the esterified products of the present invention, are tetra-valent alcohols, and the esterified products thereof with the fatty acids are obtained in the form of monoesters, diesters, triesters or tetraesters. However, the esterified products in the form of di- or higher-esters are more preferable on the average for the cold-rolling oils for steel plates according to the present invention.

The synthetic esters of the present invention may be used as the rolling oils alone or in admixture with other base oils such as mineral oil or animal and vegetable oils and fats. Further, they may be used in the form of an emulsion obtained by adding an emulsifying agent thereto.

In addition, the synthetic esters of the present invention may be used in combination with emulsifying agents, fatty acids, antioxidants and corrosion inhibitors ordinarily used as additives with mineral oils or animal and vegetable oils and fats or practical rolling oils which are usually used as the base oils.

When the synthetic ester compounds of the present invention are used in admixture with other base oils, stable properties are achievable by addition thereof in an amount of at least 5 weight %, preferably at least 20 weight %, although they are effective in an amount of as small as 1 weight %.

The materials of the present invention are applicable not only to the cold-rolling oils for steel plates but also to a wide range of industrial lubrication applications inclusive of processing or mechanical lubrication where they are used as cutting or grinding oils.

15 EXAMPLES

In what follows, the synthesis examples and examples of the present invention will be given for the purpose of illustration alone.

20

Synthesis Example 1

Into a four-necked flask having a stirrer, a thermometer, a nitrogen gas-feed tube and a water separator, 522 g (2 moles) of tris(2-hydroxyethyl)isocyanurate and 1269 g (5.85 moles) of coconut oil fatty acid were charged together, and xylene was added as a reflux solvent in an amount of 5 % of the starting materials. The mixture was well agitated and allowed to react at 160 to 230°C in the absence of any catalyst until the calculated amount of water was distilled out. The required time was 9 hours. After the completion of the reaction, xylene was distilled off under reduced pressure, followed by decoloring and filtration with activated clay, thereby to obtain a yellow liquid. The yield and acid number was 1661 g and 1.8, respectively. In similar procedures, a number of synthetic esters were prepared. The properties of the obtained synthetic esters are also set forth in Table 1.

Examples 1-7

35

Estimation was made of the lubricating and annealing properties of the rolling oil compositions obtained by adding to mineral and palm oils used as the base oils for practical rolling oils ordinarily used additives such as emulsifying agents, fatty acids and antioxidants, and the synthetic esters that were the rolling oils of the present invention.

To make estimation of the rolling lubricating properties of each rolled material under test (spcc) of 1.2X20X200 mm, emulsion rolling was carried out with a two-stage roll type rolling mill at an oil concentration of 3 % and bath temperature of 50°C, and a rolling load was then measured at a reduction ratio of 40 %. To make estimation of the annealing properties of each sample, several tens steel plates rolled with the emulsion liquid under test were formed as such into a stack, which was then fixed in place with a narrow steel belt, followed by annealing in an annealing furnace of a small size.

Referring to the heating conditions for annealing, the stack was heated in an atmosphere of 120 ml/min of NHX gas (H₂ : 5 %) to 600°C at a heating rate of 10°C/min, retained at that temperature for 1 hours, and was allowed to stand for cooling.

Thereafter, a cellophane tape was applied over the surface of each steel plate to gather surface deposits, and was stucked over white paper to visually observe the degree of contamination and thereby make estimation of the surface cleanability thereof. The results of testing are set forth in Table 2, wherein the marks are the same as those in Table 1.

55

Table 1

Sample Marks	Types of Synthetic Esters				Properties of Synthetic Esters	
	Fatty Acids	Molar Ratio	Types of Nitrogen- Containing Polyols		Acid Value	Hydroxyl Value
			X	n		
A ₁	Coconut oil Fatty acid	3	H	1	1.8	7
B ₁	2-ethylhexanoic acid	3	H	1	1.2	4
C ₁	Tallow fatty acid	3	H	1	2.1	15
D ₁	Isostearic acid 1)	3	H	1	2.3	11
E ₁	Hardened fish oil fatty acid 2)	2.5	H	1	1.5	33
F ₁	Tall oil fatty acid	3	H	1	1.9	10
G ₁	Crude methyl- branched, mixed fatty acid 3)	2	H	1	0.7	61
H ₁	Tallow fatty acid	1.5	H	1	0.9	117
I ₁	Isostearic acid	1.5	H	1	1.1	113
J ₁	Tallow fatty acid	1.0	H	1	0.5	201
K ₁	Tallow fatty acid	3	CH ₃	1	1.9	9
L ₁	Coconut oil fatty acid	3	H	3	2.5	12
M ₁	Isostearic acid ¹⁾	2	CH ₃	8	3.5	28

1) Emersol 875 manufactured by Emery

2) Hydrogenated, refined fish oil fatty acid

3) Mixed fatty acid containing methyl-branched fatty acid
formed as by-product, when preparing dimer acid from tall
oil fatty acid (SV 173, IV 70)

Table 2

		EMULSION 5)									
		Comp. Ex.		Example							
		1	2	1	2	3	4	5	6	7	
Composition of rolling oil in weight %	Synthetic ester	-	-	A ₁ 45	C ₁ 45	D ₁ 45	F ₁ 45	G ₁ 45	H ₁ 45	I ₁ 45	6)
	Mineral oil	55	65	49	50	49	49	49	50	48.5	
	Palm oil	40	25	-	-	-	-	-	-	-	7
	Stearic acid	2	7	2	2	2.5	2	3	2.5	2	
	Antioxidant 1)	1	1	1	1	1	1	1	1	1	
	Emulsifying agent 2)	2	2	3	2	2.5	3	2	1.5	1.5	
Lubricating properties	Rolling load ratio 3)	1.00	1.03	0.98	1.00	0.97	0.97	0.92	0.95	0.93	
Surface cleanliness in 4) the annealing step		△	○~△	◎~○	◎	◎	◎~○	◎	◎~○	◎~○	

1) Antioxidant: 2,6-tert-butylphenol

2) Emulsifying agent: polyoxyethylenealkylphenyl ether (HLB 11.7)

3) Rolling load ratio: value based on Comp. Ex. 1

4) Estimation of surface cleanliness:

◎: No contamination found

○: Extremely limited contamination found

5

10

15

20

25

30

35

40

45

50

55

△: Contamination found

X: Increased contamination found

- 5) Marks $A_1 \sim I_1$ indicate the same ester components as those shown by the marks in Table 1. The concentration is 45 %. The actually used rolling liquid is an emulsion having an oil content of 3 %.
- 6) The ester shown by I_1 has a concentration of 40 %.

Synthesis Example 2

Into a four-necked flask having a stirrer, a thermometer, a nitrogen gas-feed tube and a water separator, 292 g of N,N,N',N'-tetrakis(2-hydroxypropyl)ethylenediamine and 840 g of coconut oil fatty acid were charged together with 2.2 g of a catalyst toluenesulfonic acid, and xylene was added as a reflux solvent in an amount of 5 % of the starting materials. The mixture was well agitated and allowed to react at 160 to 230°C until the calculated amount of water was distilled out. The required time was 8 hours. After the completion of the reaction, the reaction product was washed with water for removal of the catalyst, and xylene was distilled off under reduced pressure, followed by decoloring and filtration with activated clay, thereby to obtain a yellow liquid. The yield and acid number were 970 g and 2.3, respectively (Sample A). In similar procedures, a number of synthetic esters were prepared. The properties of the obtained synthetic esters are also set forth in Table 3.

15

20

25

30

35


40

45

50

55

Table 3

Sample Marks	Type of Polyols			Fatty Acids		General Properties of Esters	
	X	n	R ₂	Type	Number of Moles	Acid Value	Hydroxyl Value
A ₂	CH ₃	1	(CH ₂) ₂	Coconut oil fatty acid	4	2.3	8
B ₂	CH ₃	1	(CH ₂) ₂	Isostearic acid ¹⁾	2	0.5	121
C ₂	CH ₃	3	(CH ₂) ₂	Tallow fatty acid	3	0.7	37
D ₂	CH ₃	3	(CH ₂) ₂	Hardened fish oil fatty acid ²⁾	2.5	0.6	54
E ₂	H	1	(CH ₂) ₂	Isooctylic acid	4	1.1	6
F ₂	H	1	(CH ₂) ₂	Tall oil fatty acid	3	0.5	51
G ₂	H	2	(CH ₂) ₂	Isostearic acid ¹⁾	3.5	0.5	15
H ₂	H	1	(CH ₂) ₂	Tallow fatty acid	1.5	0.4	201
I ₂	CH ₃	1	(CH ₂) ₆	Lanolin fatty acid	3	2.5	33
J ₂	H	1		Coconut oil fatty acid	3.5	1.1	18
K ₂	CH ₃	10	(CH ₂) ₂	Isostearic Acid	3.5	1.8	9

1) Emersol 871 manufactured by Emery

2) Hydrogenated, refined fish oil fatty acid

Examples 8-13

Estimation was made of the lubricating and annealing properties of the rolling oil compositions obtained by adding to mineral and palm oils used as the base oils for practical rolling oils ordinarily used additives such as emulsifying agents, fatty acids and antioxidants, and the synthetic esters that were the rolling oils of the present invention.

To make estimation of the rolling lubricating properties of each rolled material under test (spcc) of 1.2X20X200 mm, emulsion rolling was carried out with a two-stage roll type rolling mill at an oil concentration of 3 % and a bath temperature of 50°C, and a rolling load was then measured at a reduction ratio of 40 %. To make estimation of the annealing properties of each sample, several tens steel plates
 5 rolled with the emulsion liquid under test were formed as such into a stack, which was then fixed in place with a narrow steel belt, followed by annealing in an annealing furnace of a small size.

Referring to the heating conditions for annealing, the stack was heated in an atmosphere of 120 ml/min of HNX gas (H_2 : 5 %) to 600°C at a heating rate of 10°C/min, retained at that temperature for 1 hours, and was allowed to stand for cooling.

10 Thereafter, a cellophane tape was applied over the surface of each steel plate to gather surface deposits, and was stucked over white paper to visually observe the degree of contamination and thereby make estimation of the surface cleanability thereof. The results of testing are set forth in Table 4, wherein the marks are the same as those in Table 3.,

15

20

25

30

35

40

45

50

55

Table 4

		EMULSION 5)										
		Comp. Ex.	Example									
Composition of rolling oil in weight %	Synthetic ester Mineral oil Palm oil Palmitic acid Antioxidant 1) Emulsifying agent ²⁾	3	8	9	10	11	12	13				
		-	A ₂ 45	B ₂ 45	D ₂ 45	E ₂ 45	F ₂ 45	G ₂ 45				
		55	50	50	50.5	50	50.0	48				
		40	-	-	-	-	-	5				
		2	2	2	2	2	1.5	1.5				
		1	1	1	1	1	1	1				
		2	2	2	1.5	2	2	1.5				
Lubricating properties	Rolling load ratio ³⁾	1.00	0.94	0.92	0.96	0.95	0.93	0.93				
Surface cleanliness in ⁴⁾ the annealing step		△~X	⊙~○	⊙	⊙~○	⊙	⊙~○	⊙~○				

- 1) Antioxidant: 2,6-tert-butyl-4-methylphenol
 2) Emulsifying agent: polyoxyethylenononylphenyl ether (HLB 11.7)
 3) Rolling load ratio: value based on Comp. Ex. 1
 4) Estimation of surface cleanliness:
 ⊙: No contamination found

5
10
15
20
25
30
35
40
45
50
55

○: Extremely limited contamination found

△: Contamination found

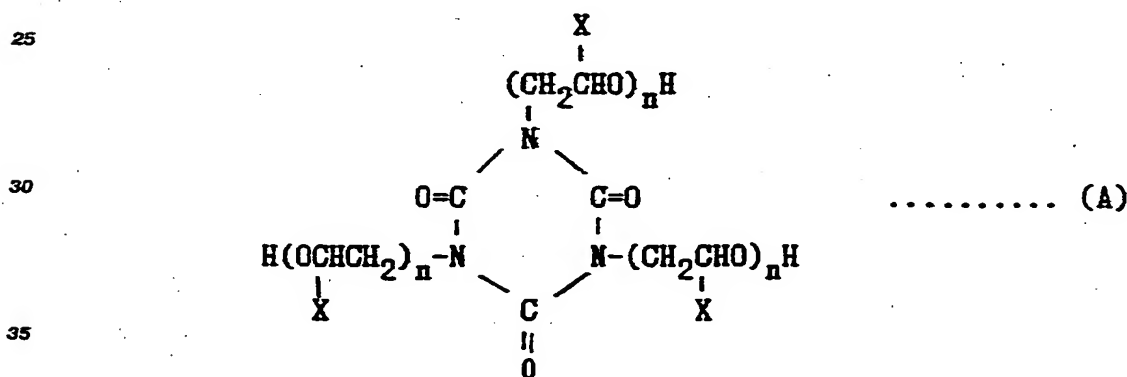
×: Increased contamination found

5) The actually used rolling liquid is an emulsion having an oil content of 3 %. Marks $A_2 \sim G_2$ show the same ester components as those shown by the marks in Table 3.

In the present invention, the synthetic ester compounds obtainable from tri- or higher-valent alcohols having tertiary nitrogen such as isocyanuric derivatives or ethylene or propylene oxide addition products of ethylenediamine are intended for use as the rolling lubricants for steel plates, and are "molecularly designed" taking into consideration the requirements to that end. Unlike the existing synthetic esters used as cold-rolling oils or additives, the ester compounds according to the present invention give rise to improvements in the rolling lubricating properties of steel plates, and make a great deal of contribution to energy and material savings such as reductions in the power cost, as compared with the conventional base oils comprising palm oil. In addition, the ester compounds of the present invention excel in mill cleanability, and can dispense with conventional electrolytic degreasing, resulting in reductions in the installation cost.

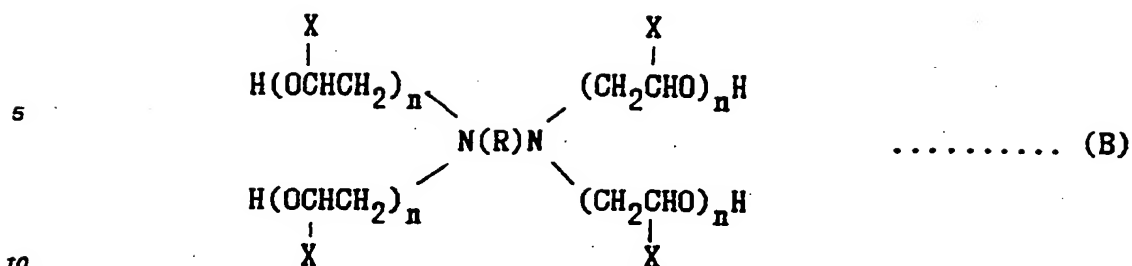
Claims

1. A cold-rolling oil for steel plates containing an esterified production of (A) a tri- or higher-valent alcohol selected from amino alcohols having tertiary nitrogen, and (B) a fatty acid having six or more carbon atoms.
2. A cold-rolling oil as recited in Claim 1, wherein the tri- or higher-valent amino alcohols having tertiary nitrogen are at least one selected from the group consisting of triethanolamine, triisopropanolamine, N,N-bis-(2-hydroxypropyl)-ethanolamine, N,N-bis-(2-hydroxyethyl)-isopropanolamine, triethanolamine tris-glycoether, tripropanolamine tris-glycoether, tris(2-hydroxyethyl)isocyanurate and tris(2-hydroxypropyl)isocyanurate.
3. A cold-rolling oil as recited in Claim 1, wherein the tri- or higher-valent amino alcohols having tertiary nitrogen are isocyanuric derivatives expressed in terms of the following general formula (A):



wherein X is H or CH₃, and n is an integer of 1 to 10.

4. A cold-rolling oil as recited in Claim 3, wherein the isocyanuric derivatives expressed in terms of the formula (A) are tris(2-hydroxyethyl)isocyanurate or tris(2-hydroxypropyl)isocyanurate.
5. A cold-rolling oil as recited in Claim 3, wherein the esterified products are obtained by esterification of 1 mole of tris(2-hydroxyethyl)isocyanurate with the fatty acids in a proportion of at least 1.5 moles on the average.
6. A cold-rolling oil as recited in Claim 5, wherein the fatty acids are esterified in a proportion of at least 2 moles on the average.
7. A cold-rolling oil as recited in Claim 5, wherein the fatty acids are at least one selected from the group consisting of coconut oil fatty acid, 2-ethylhexanoic acid, tallow fatty acid, isostearic acid, hardened fish oil fatty acid, tall oil fatty acid and crude methyl-branched, mixed fatty acid.
8. A cold-rolling oil as recited in Claim 1, wherein the tri- or higher-valent amino alcohols having tertiary nitrogen are tetra-valent alcohols expressed in terms of the following general formula (B):



wherein X is H or CH₃, n is an integer of 1 to 10, and R is an alkyl having 2 to 6 carbon atoms, a phenyl group or a cyclohexyl group.

9. A cold-rolling oil as recited in Claim 1, wherein the tri- or higher-valent amino alcohols having tertiary nitrogen are at least one selected from the group consisting of N,N,N',N'-tetrakis(2-hydroxyethyl)ethylenediamine and N,N,N',N'-tetrakis(2-hydroxypropyl)ethylenediamine.

10. A cold-rolling oil as recited in Claim 8, wherein the esterified products are obtained by esterification of 1 mole of N,N,N',N'-tetrakis(2-hydroxypropyl)ethylenediamine with the fatty acids in a proportion of at least 2 moles on the average.

11. A cold-rolling oil as recited in Claim 10, wherein the fatty acids are esterified in a proportion of at least 3 moles on the average.

12. A cold-rolling oil as recited in Claim 11, wherein the fatty acids are at least one selected from the group consisting of coconut oil fatty acid, isostearic acid, tallow fatty acid, hardened fish oil fatty acid, isooctylic acid, tall oil fatty acid and lanolin fatty acid.

⑫

EUROPEAN PATENT APPLICATION

⑲ Application number: 87200743.0

⑳ Date of filing: 17.04.87

⑤① Int. Cl.4: **C10M 105/62** , **C10M 105/66** ,
C10M 105/70 , **C10M 111/02** ,
C10M 173/00 , **C10M 133/08** ,
C10M 133/14 , **C10M 133/40** ,
//**C10N40/24** , (**C10M111/02** ,
105:62)

③① Priority: **21.04.86 JP 90098/86**
18.09.86 JP 218102/86
26.08.86 JP 198108/86

④③ Date of publication of application:
28.10.87 Bulletin 87/44

⑥④ Designated Contracting States:
BE DE FR GB IT NL

⑥⑥ Date of deferred publication of the search report:
17.08.88 Bulletin 88/33

⑦① Applicant: **The Nisshin Oil Mills, Ltd.**
23-1, 1-chome Shinkawa Chuo-ku
Tokyo(JP)

Applicant: **NIPPON STEEL CORPORATION**
6-3 Otemachi 2-chome Chiyoda-ku
Tokyo 100(JP)

⑦② Inventor: **Tanikawa, Kelichi**
34-7, Konandai 1-ch. Konan-ku
Yokohama-shi Kanagawa(JP)
Inventor: **Higaki, Yuzo**
1143-3, Kogasaka
Machida-shi, Tokyo(JP)
Inventor: **Goto, Hiroyuki**
27-9, Mori 6-chome Isogo-ku
Yokohama-shi Kanagawa(JP)

⑦④ Representative: **Noz, Franciscus Xaverius, Ir.**
et al
Boschdijk 155
NL-5612 HB Eindhoven(NL)

⑤④ Cold-rolling oils for steel plates.

EP 0 242 925 A3

⑤⑦ Lubricating oils for rolling of steel plates, which are composed of synthetic ester compounds obtainable from tri- or higher-valent alcohols having tertiary nitrogen such as isocyanuric derivatives or ethylene oxide addition products of ethylenediamine and fatty acids, possess well-balanced rolling lubricating properties and mill cleanability at a high level.



DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.4)
X	GB-A-2 024 855 (MOBIL OIL) * Claims 1-4; page 1, lines 1-9; page 2, lines 1-18 *	1,2	C 10 M 105/62 C 10 M 105/66 C 10 M 105/70
X	GB-A-1 593 891 (REEF TECHNICAL DEVELOPMENTS) * The whole document *	1,2	C 10 M 111/02 C 10 M 173/00 C 10 M 133/08 C 10 M 133/14 C 10 M 133/40 //
X	US-A-3 105 824 (GREEN et al.) * Example 3; claims; column 1, lines 1-43 *	1,8-10	(C 10 M 111/02 C 10 M 105:62 C 10 M 105:66 C 10 M 105:70)
X	FR-A-2 143 141 (HOOKER CHEM. CORP.) * Claims; page 3, lines 1-19 *	1	C 10 N 40:24
A	---	2,8	
X	CHEMICAL ABSTRACTS, vol. 103, no. 2, July 1985, page 148, no. 8809m, Columbus, Ohio, US; & CS-A-227 132 (BURYAN, PETR et al.) 01-01-1985 * Abstract *	1,2	
P	EP-A-0 206 998 (CIBA-GEIGY AG) * Abstract; claims 1,5,7 *	1	
X	US-A-3 637 557 (LITTLE) * The whole document *	1,2-7	
A	EP-A-0 143 444 (NIPPON OIL AND FATS CO.) * Claims *	1,8	
	---	-/-	
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 17-05-1988	Examiner DE LA MORINERIE B.M.S.E.
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons ----- & : member of the same patent family, corresponding document	

EPO FORM 1503 03.82 (P0401)



DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.4)
A	CHEMICAL ABSTRACTS, vol. 98, no. 12, March 1983, page 161, no. 92321e, Columbus, Ohio, US; & JP-A-57 151 700 (SANYO CHEMICAL INDUSTRIES LTD. NIPPON SYNTHETIC CHEMICAL INDUSTRY CO., LTD.) 18-09-1982 ---	1,2	
A	DE-A-2 440 531 (EDWIN COOPER & CO.) * Claims * -----	1,8	
			TECHNICAL FIELDS SEARCHED (Int. Cl.4)
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 17-05-1988	Examiner DE LA MORINERIE B.M.S.E.
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			

EPO FORM 1503 01.82 (P0401)